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A RATIONALE FOR EVALUATION AND SELECTION OF ANTIOXIDANTS FOR PR--ETC(U)
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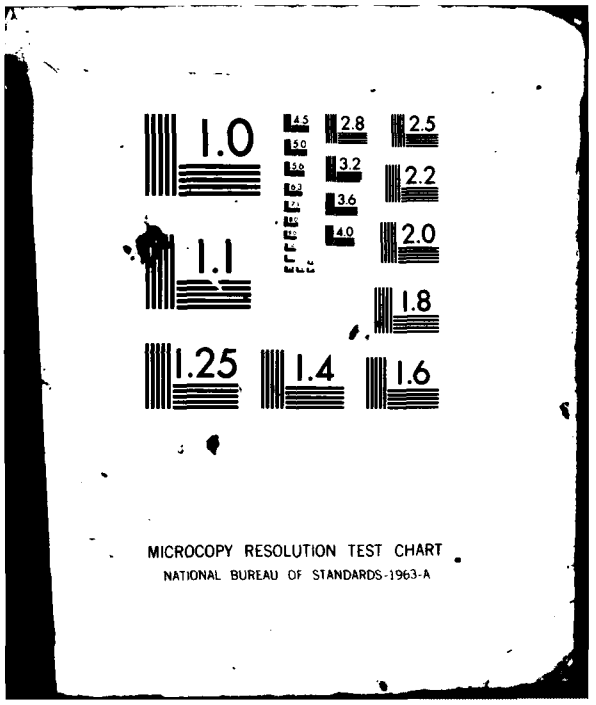
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PORTER, KAPSALIS, WETHERBY, DROLET, BLACK

A RATIONALE FOR EVALUATION AND SELECTION OF ANTIOXIDANTS FOR PROTECTION OF RATION ITEMS OF DIFFERENT TYPES U

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1. INTRODUCTION

Rancidity resulting from autoxidation of lipids (oxidation with atmospheric oxygen) in military ration items is a prime cause of rejection. Odor, color, flavor, and texture are degraded. For nearly fifty years scientists have searched for effective antioxidants and means of rating this effectiveness (1-4).

For the first forty years fats and oils were the lipids scrutinized. These are triglycerides of varying composition and are usually an artefact food, being expressed or extracted from plant or animal tissue. Frying oils, salad oils, lard and butter are examples. They have a low surface to volume ratio (LSV) and usually a low water content. Antioxidants were chosen for effectiveness in fats and oils and rated by accelerated shelf life tests using dry bulk fat or oil: the so-called Active Oxygen Method (AOM), Schaal Oven Test, and Oxygen Bomb Test. An antioxidant was considered uniformly good or bad, judged by these tests, with little regard for appropriateness in other lipids.

For the last twenty years, there has been growing attention to the protection of lipids dispersed in processed, whole tissue foods and in combination foods like baked goods, instant foods, and emulsions of the salad oil and whipped topping type. (5-13) This has been hastened by people's desire for quickly prepared convenience foods like TV or airline dinners, largely precooked and predisposed to autoxidation. The first oxidizing lipids in these foods are often polar lipids, like the phosphatides of membranes, or alternatively, highly emulsified triglycerides as in baked goods or whipped toppings. There is a characteristic high surface-to-volume ratio (HSV) and a preponderance of water as the continuous phase. The prevailing use of polyunsaturated triglycerides in these systems favors autoxidation. Chemically, the previous concentration on bulk systems, supposedly mixed and homogeneous, has given way to an interest in high surface systems, biphasic in nature with water or air as the continuous phase. Appropriate tests for antioxidants here are emulsions or dry high surface area systems. We have found that antioxidants can no longer

be considered as uniformly effective, but vary in effectiveness, depending on the food situation.

Thus people's current desires for pre-processed convenience foods have changed the practices of antioxidant use and forced a hard look at new chemical principles supporting these practices. From an empirical, state-of-the-art method of choice, this laboratory has developed a broad scientific rationale for choice of appropriate antioxidants. This paper concerns that rationale, which, it should be noted, concerns only primary antioxidants, i.e., those that function by electron or hydrogen donation to interrupt free radical chains.

2. CHEMISTRY AND TYPES OF ANTIOXIDANTS

2.1 Chemistry of Autoxidation. Characteristic of the early years and the preoccupation with supposedly mobile, mixed and homogeneous lipid systems was the confident application of classical kinetic methods. Even oxidizing bulk oils are not now considered so homogeneous because of the importance of surface oxidation. Classical kinetics is even more suspect when applied to complicated whole food systems, where concentration is ill-defined because of anchoring of components and the preponderance of surfaces. However, certain model reactions must occur in any autoxidizing system and in its antioxidant termination. A few of the most important reactions and their relative rates are shown in Figures 1, 2, and 3 (12). The first, non-free radical step (Fig.1) is considered to be the addition of singlet oxygen (often generated by a photosensitizing catalyst like traces of chlorophyll or heme). This produces hydroperoxide, which may then be reductively split by trace metal as in Reaction 2 (5). Reaction 3 produces alkyl radical from activated methylene groups in unsaturated fatty acids. The well-known chain reactions of Figure 2 propagate the reaction. Radicals from ineffective antioxidants (not well stabilized by steric or resonance means) can cause chain transfer as in Reaction 3. Termination occurs by electron or hydrogen donation as in Figure 3, where AH is a well-stabilized antioxidant and BH is less so. A type of regenerative synergism is shown in Reaction 3, typical of the interaction between water-soluble reductones like ascorbic acid and more lipophilic primary antioxidants like the tocopherols or 3-t-butyl hydroxyanisole (BHA, Fig.4).

Stabilization of the antioxidant free radical resulting from the termination step is critical and may be accomplished both by steric hindrance and resonance as in the monohydric (and lipophilic) antioxidants like BHA or 3,5-di-t-butyl hydroxy toluene (BHT) (Fig. 4), or predominantly by mesomeric resonance in the free radical, as for t-butyl hydroquinone (TBHQ) or propyl gallate (PG) (Fig. 4). The main resonance forms are shown in Figure 5 for hydroquinone.

2.2 Types of primary antioxidants. Figure 4 illustrates the major four FDA-permitted synthetic antioxidants. BHA and BHT are monohydric phenols, TBHQ is dihydric, and PG is trihydric. Lipophilia, as measured by oil-water partition coefficient, generally decreases to the right in the figure

REACTION	REMARKS
$-CH=CH-CH_2-CH=CH-CH_2- + {}^3O_2 \rightarrow -CH=CH-CH_2-CH(OOH)-CH=CH-$	RBH FREE RADICAL
$ROOH + M^{n+} \rightarrow RO\cdot + OH^- + M^{(n+1)+}$	LARGE FOR Fe^{++}, Cu^{++}, Co^{++}
$RO\cdot + RH \rightarrow ROH + R\cdot$	LARGE

Figure 1. Important reactions in initiation of surface autoxidation. Modified from Ref. 12

$R\cdot + O_2 \rightarrow ROO\cdot$	VERY LARGE
$ROO\cdot + RH \rightarrow ROOH + R\cdot$	INTERMEDIATE
$A\cdot + RH \rightleftarrows AH + R\cdot$	CHAIN TRANSFER - RATE VERY SMALL FOR POST HINDERED ANTIOXIDANTS

Figure 2. Important reactions in propagation. Modified from Ref. 12

$ROO\cdot + AH \rightleftarrows ROOH + A\cdot$	LARGE - HINDERED OR POLYHYDRIC ANTIOXIDANT
$ROO\cdot + BH \rightarrow ROOH + B\cdot$	LARGER - UNHINDERED MONOHYDRIC ANTIOXIDANT
$AH + B\cdot \rightleftarrows A\cdot + BH$	PRIMARY SYNERGISM - RATE SMALL

Figure 3. Important reactions in termination by antioxidants Modified from Ref. 12

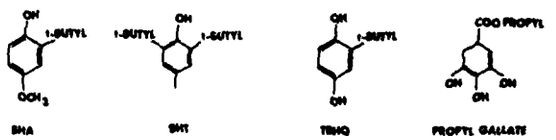

Figure 4. The major synthetic antioxidants in common food use. Ref. 24

although BHT is slightly more lipophilic than BHA. Both BHA and BHT are largely non-polar and are practically insoluble in water, while PG partitions about evenly between water and triglyceride (Table 1) (12). None of these have notable surface activity or amphiphilia, although TBHQ and PG have somewhat separated lipophilic and hydrophilic moieties.

Figure 6 illustrates the generic dihydric and trihydric phenols, whose substituted derivatives form the vast majority of antioxidant compounds found in nature. In particular, the ortho dihydric structure of catechol is found in the ubiquitous caffeic acid of coffee and oats, and the trihydric pyrogallol structure in gallic acid of tannins. The hydroquinone moiety occurs in flavonoids. All of these structures tend to be polar and hydrophilic, particularly as the salts of phenolic acids or the glycosides of flavonoids. Figure 7 shows some natural monohydric phenols which are antioxidants, like the abundant tocopherols. The three shown are volatile and highly flavored or pungent, but are very effective antioxidants in appropriate situations. Except for the tocopherols, lipophilic antioxidants are much less common than hydrophiles in nature, and often are volatile flavorants.

2.3 Solubility and surface activity. Substantial lipophilia can be conferred on any polar antioxidant moiety by the addition of a lipophilic side chain group, whether naturally occurring or synthetic. The long chain alkyl gallates are an example (Table 2) (25), lipophilia increasing exponentially with each added methylene or congener group. In addition, the molecules so formed possess amphiphilia, or surface energy, since they possess a pronounced polar moiety separated from a non-polar one. One measure of this tendency is the so-called "Hydrophilic-Lipophilic Balance" number, used in detergent formulation(14). In a surface active molecule, a large HLB number connotes greater water solubility and a tendency to form oil-in-water emulsions. Conversely, a low HLB number is associated with greater lipophilia. Although low HLB is associated with lipophilia in surface active compounds, the higher molecular weights preclude the volatility one might expect.

3. AUTOXIDATION AND ANTIOXIDANTS IN LOW SURFACE TO VOLUME RATIO (LSV) LIPID EXPOSURES

As was noted above, the autoxidation and antioxidant protection of bulk fats and oils was largely the target of the first forty years of effort. These are characterized by LSV exposure, by non-polar lipids, and a dry, non-polar environment. The compounds are triglycerides, which are often less polyunsaturated and oxidation prone than polar phosphatides. Above their melting point, which is the case in the typical antioxidant test for dry oils, they are mobile, mixed, and homogeneous on a macro scale. Such a test is the AOM (Active Oxygen Method), where air is bubbled through the oil at 100°C until peroxide value 70 is reached. For this situation we have found that, paradoxically, other things being equal, antioxidants of greater hydrophilia or ampiphiles of higher HLB are more effective than the lipophiles like BHA, BHT, and the tocopherols.

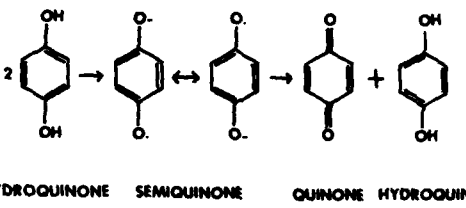

Figure 5. Semiquinone stabilization and dismutation
Ref. 24

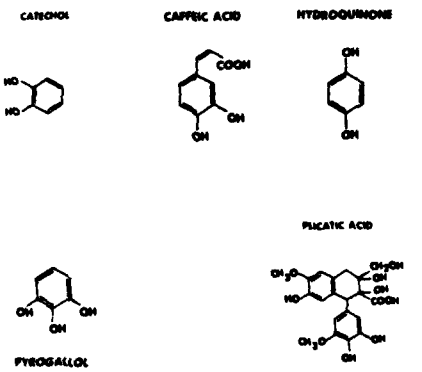

Figure 6. Dihydric and trihydric phenols.
Ref. 24

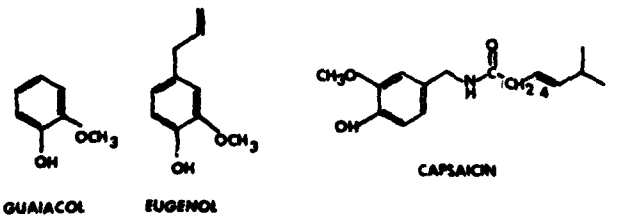

Figure 7. Volatile monohydric phenols.
Ref. 24

TABLE 1. Solubility of Antioxidants[a]

Solvent	BHT	BHA	TBHQ	PG
Water	Insol.	Insol.	<1	<1
Glycerol	Insol.	1	ca. 5	25
Propylene Glycol	Insol.	70	30	55
Methyl Linoleate	V. Sol.	V. Sol.	>10	1
Corn Oil	40	30	10	Insol.
Lard	50	40	5	1

[a]Ref. 12

TABLE 2. Butteroil/Water Partition Coefficient of Antioxidant at 40°C[a]

Antioxidant	Water	Milk Salt Solution
Ethyl Gallate	0.24	-
Propyl Gallate	1.33	0.84
Isopropyl Gallate	0.64	-
Butyl Gallate	5.8	3.9
Amyl Gallate	18.5	9.5
Hexyl Gallate	71.0	44.8
Nordihydroguaiaretic Acid	21.7	21.4
Butylated Hydroxyanisole	834	825

[a]Ref. 25

TABLE 3. Effect of Increasing Alkyl Chain Length on Antioxidant Activity of Substituted Hydroquinones[a]

Antioxidant (0.05 Wt % in Safflower Oil)	Oil Life (Time to PV 70)[b] AOM at 210°F Hours	Storage at 110°F Days
None (Control)	9	21
Hydroquinone	39	191
Methylhydroquinone	69	330
Pentylhydroquinone	50	203
Octylhydroquinone	46	208
Dodecylhydroquinone	34	162

[a]Ref. 26

[b]Meq. peroxide/kg oil

Evidence for this "polar paradox" comes from tests of several homologous series of increasingly alkylated phenols. Innate potency of a given phenolic moiety results from a complicated balance of low reduction potential (hydrogen-donating tendency), high rate and low activation energy for the termination reaction (Fig. 2), and low chain transfer rate (steric hindrance and mesomeric resonance of the alkoxide free radical), among other factors. A homologous series with the same antioxidant moiety normalizes these effects and permits comparison of the effect of lipophilia or amphiphilia alone on effectiveness.

The lipophilic monohydric phenols like BHA, BHT, and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (SANTOQUIN™) show very little to no activity in vegetable oils in AOM tests. The writer knows of no homologous series with these monohydric moieties. For the very active dihydric alkylated hydroquinone series, Table 3 (26) shows the relative effectiveness in AOM tests on safflower oil. Strictly speaking, hydroquinone itself is not a homologue, but in the remainder of the series, as lipophilia increases, activity declines with increasing chain length on a weight basis and remains virtually constant on a molar equivalent basis. It seems noteworthy also that hydroxyhydroquinone--again, not a strict member of this series, although exceedingly polar and water soluble--is the most effective of all hydroquinones tested in the AOM (89 hours).

Similar results for the ortho trihydric gallates are shown in Table 4 (26,27), where the low HLB dodecyl gallate has virtually no effect on induction period. Again, gallic acid is not a strict homologue of the rest of the series, but it is the most polar and water soluble and the most effective antioxidant in these dry oils. 1-galloyl glycerol, an even more highly polar compound, is even more effective in the AOM (15). Table 2 shows the oil/water partition ratios of these gallates and BHA.

Table 5 (28) shows similar partial homologous series for the ortho dihydric caffeic acid and for the mono-methoxylated analogue, ferulic acid. The same trend is evident, this time in oat oil. Several other series show similar trends. There are few exceptions to the rule that in dry vegetable oils and lard, the most polar member of a homologous series is the most effective antioxidant on a weight basis. Even on a molar equivalency basis, alkylation and lipophilia confer no advantage in this very non-polar exposure. In animal lard, the monohydrics BHA, BHT, and tocopherol show substantial activity in the AOM test, but the more polar dihydric and trihydric phenols remain superior (16).

4. HIGH SURFACE TO VOLUME LIPID EXPOSURES: EMULSIONS, MEMBRANES, DEHYDRATED FOODS

It was first noticed by Chipault (17) and by Uri(18,5) that antioxidants behave differently in emulsions than in dry oils. We at Natick Laboratories became interested in autoxidation in high surface situations in the early Sixties because of the large use of freeze-dried foods in stored military rations. Like several other workers(19-22) we have moved from carefully controlled simple model systems (linoleic acid in monolayer on

TABLE 4. Effect of Increasing Length of Alkyl Chain on Antioxidant Activity of Gallic Acid Esters

Antioxidant Treatment of Oil (% by Wt)	AOM Stability of Vegetable Oil (Hours to PV 70)					
	Cotton Seed[a]			Safflower[b]		
	Wt %	AOM	Control	Wt %	AOM	Control
Gallic Acid	-	-	-	0.05	27	9
Propyl Gallate	0.01	19	9	0.05	24	9
Hexyl Gallate	-	-	-	0.05	22	9
Octyl Gallate	0.01	11	8	-	-	-
Dodecyl Gallate	0.01	10	8	-	-	-

[a]Ref. 27

[b]Ref. 26

TABLE 5. Effect of Increasing Length of Alkyl Chain on Antioxidant Activity of Esters of Caffeic and Ferulic Acid[a]

Antioxidant (1 mg/100 mg oil)	Antioxidant Activity Oat Oil - Increase in Induction Period (Hrs/@100°C)
Control	(2)[b]
Caffeic Acid	90
Ethyl Caffeate	49
Dodecyl Caffeate	29
Hexacosyl Caffeate	29
Ferulic Acid	14
Hexacosyl Ferulate	*2*
Propyl Gallate	60

[a]Ref. 28

[b]Control shows actual induction period, not increase.

TABLE 6. Relative Effectiveness of Antioxidants in RBC Ghosts Perfusion Uptake Method - More Effective Compounds[a]

Compound	Mean Relative Effectiveness (REFF)	Mean Deviation[b]
Octadecyl Gallate	134	± 8
Topanol 354[c]	19	0.1
	60<REFF<90[e]	Indefinite[d]
Phytyl Gallate	20<REFF<55[e]	Indefinite[d]
	53	5
BHA	15	1.1
	10	1.2
TBHQ	4.4	0.3
	5.0	0.2
α-Tocopherol	3.6	0.8
	4.7	1.2

[a]Ref. 24, 30

[b]Where N = 2, except as shown. Means and deviations are for two separate experiments per compound.

[c]3,5-di-t-butyl-4-hydroxy anisole.

[d]N = 4.

[e]Induction period ended during interruption in readings.

silica gel) through more advanced systems (freeze-dried red blood cell ghosts and lecithin liposomes) to more realistic situations (freeze-dried carrots). From this work, we have found that antioxidants differ greatly in effectiveness in high surface situations from their performance in dry oils. Indeed, paradoxically, in this more polar exposure, non-polar lipophiles like BHA, BHT, and Santoquin or low HLB amphiphiles are favored. Thus, the higher alkyl homologues in a series outperform the more polar lower members in protection of emulsions and membranes.

Antioxidant tests for this HSV exposure include oxygen uptake from freeze-dried or organic solvent-freed systems deposited on supports of high specific area like silica, carboxymethylcellulose, or microcrystalline cellulose. Emulsion tests may be monitored by spectrophotometry, polarography, or fluorescent detection of malonaldehyde. The systems are often characterized by a large excess of the continous phase, water, or the air space remaining after dehydration or organic solvent removal.

4.1 Linoleic Acid Monolayers on Silica. Our first work employed monolayers (Langmuir equivalent) of linoleic acid deposited under equilibrium conditions from petroleum ether solution, the excess of which was removed by decantation and a final dry nitrogen stream. Oxidation was conducted at 80°C in glass vessels closed with a rubber serum bottle stopper permitting headspace gas sampling. Oxygen content was determined on a gas partitioner. Under these conditions, pure linoleic acid autoxidizes in an apparent first order manner with no induction period, (29,32) unlike its behavior in low surface situations. Antioxidants pre-deposited on the activated silica from alcohol produce an induction period (time to an arbitrary oxygen uptake) and relative effectiveness (REFF) can be stated as

$$REFF \approx \frac{I_a}{I_c} - 1$$

where I_a = time to stated oxygen uptake with antioxidant

I_c = time without antioxidant

Figure 8 shows the apparent kinetics of oxygen uptake and the large relative effectiveness of BHA in contrast to the more polar caffeic acid and propyl gallate.

4.2 Red blood cell ghosts. We moved next to hemoglobin-free red blood cell ghosts, produced by the Dodge, Mitchell, Hanahan (23) method at pH7.4 in phosphate buffer. Ghosts are freeze-dried and for an antioxidant test are rehydrated by shaking for one hour at 20°C at 1 mg/ml in 20 mM phosphate buffer, pH 7.4, with or without antioxidants introduced from alcohol at 0.025 mg/ml final concentration in the buffer. The ghosts are centrifuged and washed in de-ionized water. Cobalt chloride is added at 0.3mg/ml and the suspension is freeze-dried. Oxygen uptake is studied by gas partition chromatography, and the results analyzed as in paragraph 4.1, above. Ghosts without cobalt are very refractory to autoxidation, but the reductive activation of peroxide by this metal promotes autoxidation strongly in these dry systems.

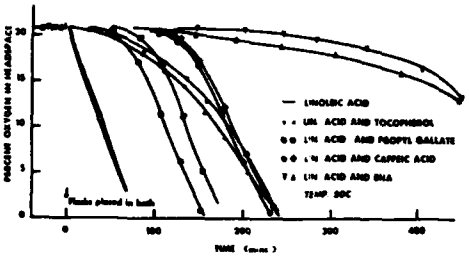

Figure 8. Effect of antioxidants on oxygen uptake of linoleic acid monolayers adsorbed on silica gel. Ref. 29.

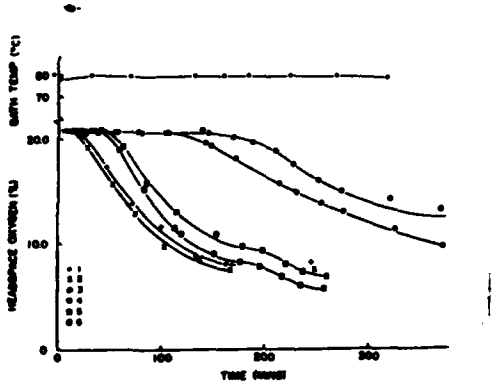

Figure 9. Effect of antioxidants on autoxidation of cobalt-activated freeze-dried red blood cell ghosts. (1,2) control; (3,4) BHA; (5,6) PG. Ref. 30.

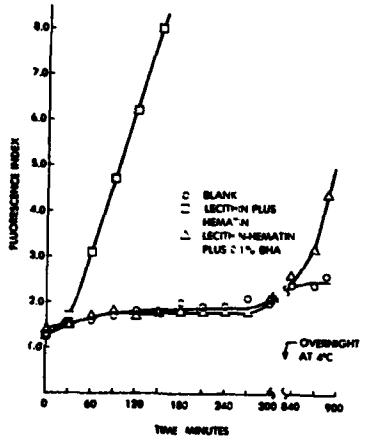

Figure 10. Antioxidant evaluation by oxidative polyamide fluorescence from soy lecithin liposomes. Ref. 31.

The superiority of BHA over propyl gallate in HSV systems is again demonstrated in Figure 9 for red blood cell ghosts. Low HLB amphiphiles are even more effective than the lipophiles BHA and Topanol 354 in this system, which is a realistic model of many whole food lipid and protein membranes. Table 6 shows this superiority and that of phytyl gallate, the phytol ester of gallic acid, synthesized by us specifically for membrane antioxidant effectiveness (24,30).

In both the silica monolayer and ghost systems, the quite volatile BHT is low in apparent effectiveness, but vapor phase uptake tests show that where it is retained in a closed system and not lost by sublimation, it is highly effective in both ghosts and freeze-dried carrots.

4.3 Lecithin liposomes. As a plant membrane model analogous to red blood cell ghosts, we have prepared sonicated soybean lecithin microdispersions and tested antioxidant activity in hematin-catalyzed samples at 65°C, monitoring autoxidation by solid sample measurement of the fluorescent compound formed between malonaldehyde (a breakdown product of peroxidized lipids) and polyamide powder.

We have used a sonicated aqueous dispersion (3 mg/ml) of either crude soybean lecithin (35% acetone solubles, largely triglyceride) or acetone-extracted soybean lecithin (3-5% acetone solubles). pH is 5.5 in 0.013M phosphate buffer. Sonication is done in a salt-ice cooled bath under a stream of dry nitrogen for a maximum of 20 minutes. Antioxidant in ethanol is added at 0.1% by weight of the dispersed lipid. The dispersions are then bubbled with glass-filtered air for thirty minutes. Hematin is added at zero time to give a final phosphatide-hematin ratio of 100/1. Twenty-five ml of the dispersion is placed in a covered Petri dish with a 2x3 cm strip of polyamide-coated plastic taped to the cover, powder side facing the solution. The dishes are placed in a 65°C draft oven and sampled at 30 minute intervals by removing the tape and reading the fluorescence in a solid sample attachment for a spectrofluorometer. Malonaldehyde arising from the oxidizing system forms an intense fluorescent amino-imino-propene compound with the amine end groups of the polyamide powder. Excitation wavelength is 360 nm and emission 425 nm. A 390 nm filter is used. A blank plate produces a characteristic diffraction pattern of bands in addition to the residual of the scattered excitation wavelength at 360 nm. The 360 scatter peak is used as an internal reference and fluorescence intensity is expressed as

$$\text{Fluorescence Index (F.I.)} = \frac{I_{430}}{I_{360}}$$

where I_{430} = intensity at 430 nm

I_{360} = intensity at 360 nm

F. I. values for both blank and sample are plotted on the same graph and their difference (ΔF.I.) is an integrative measure of malonaldehyde

produced. Kinetics of fluorescence development are similar to those found with other indices (oxygen consumption, absorption at 233 nm, etc.) as are the effects of pro-and antioxidants. Analysis of relative effectiveness is similar to that in paragraph 4.1.

Figure 10 shows the time course of fluorescence development in an antioxidant-protected and a control sample. The control shows a short induction period attributable to the residual natural antioxidants in the soybean lecithin. In this case, BHA produces a very long period with virtually no fluorescence development.

Relative effectiveness of the most effective antioxidants in the lecithin microdispersion system is shown in Table 7 (31). Table 8 (31) displays the least effective compounds. Plainly, in this very polar system with a large preponderance of water (the dispersed lipid is only 0.3% of the continuous buffer phase) the lipophiles and the low HLB amphiphiles are much more effective than the more polar and hydrophilic phenolic acids, flavonoids and hydroquinone.

The lecithin dispersion has a net anionic charge, like most natural membranes. In addition, the phenolic acids are largely ionized at ph 5.5, and would be repelled by the micelles. However, this does not explain the low activity of hydroquinone, TBHQ, quercetin and methyl gallate, each of which is highly effective in dry oil tests.

5. THE POLAR PARADOX

The preceding results can be summed up in a rationale known as the "Polar Paradox". This states that, other things being equal, more polar and/or hydrophilic antioxidants and amphiphilic antioxidants of high HLB will be more effective in dry oils of low surface-to-volume ratio (LSV) and non-polar lipophilic antioxidants or amphiphiles of low HLB will be relatively more effective in dispersed phases of high surface-to-volume ratio (HSV), like emulsions, and the membranes of whole tissue foods, whether hydrated or dehydrated.

Obviously, this is a broad generalization, and it will be modified in the individual case by particulars of molecular structure, membrane or micelle affinity, susceptibility to loss or degradation during introduction, processing or storage (the low "carry-through" of the gallates in baking due to heat and alkalinity), and by mechanical barriers to introduction in real foods. However, the trend is unmistakable and to the writer at the present time, it is the most effective rationalization of the seemingly endless particulars of state-of-the-art antioxidant use.

Figure 11 (31) summarizes graphically the contrasting results of existing AOM tests and the lecithin microdispersion tests reported here for sixteen common synthetic and natural antioxidants.

In both LSV and HSV situations, it appears that autoxidation occurs largely at surfaces. Antioxidants of equal innate potency will differ in relative effectiveness to the degree that they reach and remain at that surface.

6. APPLICATIONS OF THE RATIONALE AT NATICK LABORATORIES

We have used the rationale in choice of appropriate antioxidants for two types of whole tissue foods; restructured meats and freeze-dried carrots.

6.1 Restructured meats. For reasons of economy and portion control, at Natick, less than prime meat parts are formed into thin flakes by a centrifugal flaking machine, mixed with salt and sodium tripolyphosphate to promote myosin exudation, then frozen, compressed into "logs", and sliced into restructured "steaks" for frozen packaged storage. The flaking, like grinding of ground beef, promotes autoxidation of membrane phospholipids through release of ferrous iron from the myoglobin, and the increase of air-exposed surface. Since this is an HSV situation, BHA or BHT are expected to be very effective in prevention of the so-called "warmed-over" flavor, and such was found to be the case.

6.2 Autoxidation of freeze-dried carrots. Because of the very great increase of gas-lipid interface occasioned by the freeze-drying process and the much longer storage periods which the spoilage-free freeze-dried foods can permit, autoxidation with attendant off odors (violet from β-ionone), texture changes, and decolorization occur rather rapidly if a completely anaerobic atmosphere is not maintained. Antioxidants can be introduced by a vapor-flush technique (24), and as expected in an HSV situation, lipophiles, in this case volatile ones like BHT or eugenol are very effective for the "once-open", vapor-tight package situation.

7. SUMMARY

Selection of appropriate antioxidants for lipid-containing ration items has hitherto been largely empirical. We have developed a broad, scientifically based rationale for this purpose and are currently putting it into practice. The rule states that, other things being equal, antioxidant applications are of two general types: (1) Dry, bulk oils and fats of the cooking and salad types, whether at storage or cooking temperature, having a low ratio of surface to volume. These are best protected by polar or hydrophilic antioxidants. (2) Emulsions and membranes, with a preponderant water or gas phase and a high surface-to-volume ratio. These are best protected by lipophilic, non-polar, or amphiphilic antioxidants with a low hydrophilic-lipophilic balance number (HLB).

Application of the above rationale to model systems and natural membranes (lecithin liposomes and red blood cells) allowed us to predict its applicability to restructured meat and freeze-dried carrots.

8. ACKNOWLEDGMENTS

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TABLE 7. Relative Effectiveness of Most Effective Antioxidants in Soy Lecithin Liposomes[a]

Compound	Mean[b]	Standard Deviation	Coef. of Variation
BHA	32	± 7.8	0.24
BHT	21	8.1	0.39
Ethoxyquin (San)	13	5.6	0.43
Propyl Gallate	11	3.8	0.35
Octyl Gallate	11	7.9	0.72
Dodecyl Gallate	10	6.0	0.60
Topanol	10	6.3	0.63
Ethyl Gallate	7	5.8	0.78

[a]Ref. 31

[b]Highest three values.

TABLE 8. Relative Effectiveness of Least Effective Antioxidants in Soy Lecithin Liposomes[a]

Compound	Mean[b]	Standard Deviation	Coef. of Variation
TBHQ.	4.9	± 4.4	0.90
Quercetin	4.1	1.7	0.41
Methyl Gallate	3.2	0.4	0.13
Hydroquinone	3.2	0.9	0.28
Gallic Acid	1.4	0.3	0.21
Caffeic Acid	1.4	0.2	0.14
Chlorogenic Acid	1.4	0.2	0.14
Poly AO™79	1.1	0.2	0.18

[a]Ref. 31

[b]Highest three values

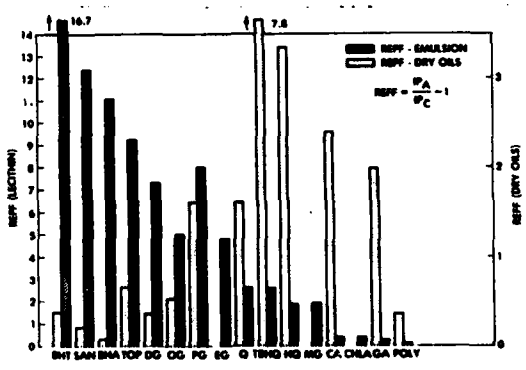

Figure 11. Relative effectiveness (REFF) of antioxidants in soy lecithin emulsions and dry vegetable oils. Ref. 31.

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